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ELECTRICAL PROPERTIES OF COATINGS AS RELATED TO PERFORMANCE. II.

EXPERIMENTS WITH SEVEN ADDITIONAL IMMERSED COATING SYSTEMS

by

Peter J. Hearst, Ph. D.

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U. S. Naval Civil Engineering Laboratory

U. S. NAVAL CIVIL ENGINEERING LABORATORY
Port Hueneme, California

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ABSTRACT

Seven coating systems on steel panels were immersed in salt water for up to nearly two years. AC and DC electrical properties of the coatings were determined and were compared with the performance of the coatings in the laboratory, in shallow water, and in the deep ocean. Four of the systems showed comparatively little deterioration, and these coatings maintained high AC and DC resistances. Two systems which showed greater deterioration in exposure to sea water had high resistances initially, but subsequently developed lower AC and DC resistances. One system, consisting only of inorganic coatings was very conductive and its electrical properties thus could not be related to performance. Long term performance data for correlation with electrical measurements are not yet available. No definite relationship between dissipation factors of the coating systems and performance could be established, nor could a relationship between water permeability and performance be established.

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INTRODUCTION

The U. S. Naval Civil Engineering Laboratory investigates and evaluates new coatings for the Naval Facilities Engineering Command, and conducts research related thereto. The evaluation of the performance of such coatings under conditions similar to those encountered in actual service requires considerable time, especially if the coatings have long service lives. There is thus a strong need for reliable accelerated test methods.

Many accelerated tests have been described in the literature.¹ However all the tests described appear to be of limited usefulness. Some tests show limited correlation for very specific applications. Others were found suitable for comparing two or three coatings without much being known about their general applicability. Two general methods show some potential promise of being useful. One of these is accelerated weathering in weathering machines, which is claimed by some to provide useful results but according to others gives poor correlation.² The other method of special interest is in assessment of potential performance by electrical measurements on coatings.³

Several authors have alleged that electrical measurements on coatings immersed in an electrolyte can be used to predict coating performance.⁴⁻¹⁰ Organic coatings with good film integrity are good insulators whereas coatings that have lost their film integrity have lost electrical properties associated with good insulators. It has been alleged that such changes in electrical properties can be detected much sooner than visual changes and that they can therefore be used to predict performance. However, no published papers really show good correlation of electrical measurements with exposure results for a large number of coatings, and the validity of the method has not been proven. Further investigations of some of the electrical methods, including measurements of DC resistance, and various AC properties, such as capacitance, resistance, and dissipation factor, are needed to determine their validity as accelerated tests.

The results of AC electrical measurements with five immersed coating systems have been reported previously.¹¹ The systems chosen for this initial study were of widely different performance in sea water. The results showed that there was appreciable correlation between the resistance and capacitance values of the coatings and the deterioration which was produced. Thus, the

system with the lowest performance, an oil paint system, was the first to show reduced resistance values. The best performing system, a Saran system, had moderately high and very steady resistance values. The other three coatings were intermediate both in performance and in the stability of the resistance values.

An additional seven coating systems on steel panels immersed in sea water have now been investigated for a period of nearly two years. In addition to AC measurements, DC electrical resistance measurements were also made. The results of these experiments are reported and discussed below.

EXPERIMENTAL METHODS AND RESULTS

The coatings that were employed were applied to steel panels 2-3/4 inches wide and 5-7/8 inches high, which were made from 1/8-inch hot rolled steel plate. The panels were sandblasted and the coating systems were applied at thicknesses of approximately 10 mils (250 microns). Before the panels were coated, handles made of 1/4-inch stainless steel strips were attached to the panels with stainless steel machine screws. The coatings were applied with a spraying machine to insure even coverage. The edges were carefully touched up during the painting operation and after the painted panels had dried, the upper portions of the panels were covered with an epoxy coating which extended down 1-3/8 inches from the top, and the other three edges were dipped 1/4-inch deep into the same epoxy coating to further protect the edges. The top portions of the panels were then brushed with molten ceresin and the edges were dipped 1/4-inch deep into molten ceresin to further insulate the edges electrically from the sea water and to reduce any edge effects in the AC measurements. The area of the coating of the nominal thickness was thus approximately 5.6 cm by 10.6 cm on each side for a total area of 120 sq cm on the two faces of the panels. Some of the panels are shown in Figures 1 and 2.

The coating systems that were employed in the present experiments consisted of zinc inorganic undercoats with a variety of topcoats (one vinyl, two epoxies, two hydrocarbon resins, and an inorganic coating) and of a comparison coating system consisting of the standard Navy vinyl-alkyd system. The systems and their thicknesses are described in Table 1.

The baths in which the panels were suspended were rectangular glass jars 8 inches wide, 11-1/2 inches long, and 8 inches high, as indicated in Figure 3. Sea water was continuously run through the baths. Aerated sea water was maintained at 25°C in a reservoir and was allowed to flow into the baths through an inlet tube extending to the bottom at one end of the jar. At the other end of the jar, approximately 2-1/4 inches from the top edge, a hole was drilled to accommodate an outlet tube. The panels were suspended

from square fiberglass rods which were placed on the top edge of the jars. The length of the hooks and the level of the sea water was such that the 120 sq cm of test surface of each panel was always immersed.

The AC electrical measurements were made with a capacitance measuring assembly consisting of a capacitance bridge, an audio oscillator, and a tuned amplifier and null detector. (General Radio model 1620). This assembly was much more accurate than the impedance bridge previously used (General Radio model 1650), especially at frequencies above 1 kc. The latter bridge, however, had to be used when conductances were higher than 111 micromhos. When the impedance bridge was used to measure parallel resistance, it was necessary to balance the circuit with an external decade capacitor.

The capacitance measuring assembly read series capacitance and dissipation factor directly and also dissipation factor and conductance. The resistance values were calculated from the conductance values. Measurements with the capacitance measuring assembly were made with three-terminal connections. A grounded lead was attached by an insulated alligator clip to the handle of the panel being measured and contact with the sea water was maintained through a cylindrical platinum screen electrode 15 mm in diameter and 50 mm high. The connection from the capacitance bridge to this electrode was also grounded. Measurement errors with this assembly were negligible, even at frequencies up to 10 kc.

The AC resistance and capacitance values of two panels of each system were obtained and these are plotted in Figures 4 to 10. The dissipation factors were also obtained but are not presented in this report. Dissipation factors versus frequency curves for the first panel of all systems, except S19, after three hours of immersion are shown in Figure 11.

DC electrical measurements were made by a modification of the methods of Bacon⁴ and of Brown.⁵ Contact to the sea water was maintained with a calomel electrode and voltage measurements were made for the system: panel/coating system/ sea water/calomel electrode. An electrometer with an input resistance of 10^{14} ohms was used (Kiethley model 610).

To obtain DC resistance values, the open circuit potential of the above system or cell was first measured. The above system was then shunted by switching to the proper amperage scale and thus reducing the input resistance of the electrometer. The new voltage was measured, and the DC resistance was calculated from the following equation:

$$R_i = \left(\frac{E_o - E_s}{E_s} \right) R_s$$

where R_i is the internal resistance of the cell (or the resistance of the coating), E_o is the open circuit potential, E_s is the shunted potential, and R_s is the shunt resistance (or input impedance of the electrometer).

When the DC resistances of the panels were greater than about 10^{10} ohms, or when the open circuit potentials were quite low, as in the control system, C1, the measured open circuit potential was increased by the addition of the voltage from a potentiometer. When measurements were made with panels of such high resistance, the time taken for the voltage reading to come to an equilibrium was further speeded by imposing, effectively at the electrometer connections, a charging potential very close to the expected equilibrium voltage. These voltages were obtained and imposed by the circuit shown in Figure 10.

In the measurement of shunted potentials, some time was required to obtain an equilibrium value. For DC coating resistances of 10^9 ohms or less, the time required to reach equilibrium was approximately two minutes. For resistances near 10^{11} ohms, approximately 20 minutes were required to reach a reasonable equilibrium value if no charging potential was employed. When the time constants were very long, or when there were fluctuations in readings due to external factors, the voltage readings versus time were plotted to arrive at better equilibrium values or average values.

System S19 (inorganic) had very low DC resistance values. The DC resistance values of the panels of this system and of other panels whose resistances were less 10^6 ohms, were measured with the platinum screen electrode in the sea water, rather than the calomel electrode, since the latter might have been damaged by the lower resistances of the shunted circuits.

The logarithms (to the base 10) of the calculated DC resistance values of all panels are plotted in the curves of Figures 13 to 19. The open circuit potentials of the first panels of all systems are shown in Figure 20.

The test panels were immersed in two sets. The first set, consisting of one panel of each system, was immersed over a period of 25 days, so that not more than one panel was immersed on any one day and that complete attention could be given to that panel. About 250 days later, the second set of panels, was immersed. It consisted of two panels of each system, and two such panels of any one system were immersed on one day.

Part of the reason for the delay between the immersion of the two sets were difficulties encountered with the DC resistance measurements. Some of these difficulties were caused by low resistances in some of the critical connections of the circuit shown in Figure 10. Part of the difficulties were caused by radiation interference from interrupted circuits in the Laboratory. The

DC resistance values initially obtained had upper limiting values near 10^9 ohms. Values obtained for the resistances of the first panel of each system for up to about 125 days were thus probably in error if they approached 10^9 ohms, and the first portions of the DC resistance curves of these panels were therefore entered as dashed lines in Figures 13 to 19.

The panels were removed from the aerated sea water monthly and were cleaned with a soft brush. They were visually rated every two months. None of the panels showed rusting in up to two years. System S14 (vinyl) developed blisters, as shown in Figure 1. System S16 (epoxy), on two of the three panels, developed one very large blister or a cluster of large blisters. System S19 (inorganic) gradually lost the topcoat by flaking off, as shown in Figure 2. The other systems showed no changes, except that they all became discolored by the brown deposits which could not be brushed off completely. The average ASTM blistering ratings for each system, at one and two years, are shown in Table 2.

A set of unscribed and scribed panels, 6 by 12 inches and coated with the above systems, had been exposed in the deep ocean on a submersible test unit at 6800 feet.¹² The panels were recovered after 13 months and were rated. The blistering ratings for the unscribed panels are shown in Table 2. No rusting was found.

Other coated panels, 4 inches wide and 10 feet long, were exposed in the Port Hueneme Harbor.¹³ These panels were so placed that they were exposed in an atmospheric zone, an intertidal zone, and an immersed zone. The blistering rating in the immersed zone, after 1- $\frac{1}{2}$ years of exposure is shown in Table 2. In addition to System S14 (vinyl) and S16 (epoxy), System S17 and S18 (both having a soft hydrocarbon topcoat) also showed some blistering. The latter blistering may have been caused by the heavy barnacle attack found on these panels. The panels showed no rusting except for a few rust spots at some edges.

Free films of the various systems were prepared by spraying on to a Teflon film stretched over a steel panel. None of the zinc inorganic silicate coatings adhered to the Teflon and, except for System C1, the free films of the coating systems were thus incomplete. For Systems S17 and S19 no good films could be obtained, and for System S18 a film of only the topcoat was obtained.

The permeabilities of the free films were determined according to ASTM method D 1653-59T with Fisher permeability cups. Water was placed in the permeability cups, and they were inverted so that the water actually touched the coating films. The cups with films and water were placed in a desiccator containing calcium chloride so that the outside humidity was essentially zero. The tests were performed at approximately 25°C. The specific permeabilities are the calculated number of milligrams of water that would penetrate a one square centimeter film one millimeter thick in 24 hours.

The specific permeabilities obtained are listed below together with the calculated permeabilities per square centimeter of the organic coatings of the systems (or of the topcoat of System S18).

<u>System</u>	<u>Specific Permeability</u>	<u>Thickness (millimeters)</u>	<u>Permeability per sq cm</u>
S14	0.073	0.18	0.41
S15	0.046	0.24	0.19
S16	0.087	0.24	0.36
S18	0.063	0.17	0.37
C1	0.085	0.27	0.31

DISCUSSION

In the first experiments on electrical properties of immersed coating systems as related to performance, five coating systems were employed whose performance was expected to differ considerably. Appreciable correlation between the resistance and capacitance values of the coatings and of the deterioration which was produced was observed. The changes in the electrical properties were compared with the performance of the small panels immersed in sea water at 25°C which were used in the electrical measurements.

It was desired for the next series of tests to compare the changes in electrical properties not only with the performance of the panels in the sea water at 25°C, but also with the performance of panels similarly coated and evaluated in an actual ocean environment. It was therefore decided to paint the test panels for electrical measurements at the same time and under the same conditions as the next set of test panels which were to be used in the evaluation of coatings in a natural environment. The systems which were being prepared for such evaluation were a series of systems with inorganic zinc primers and organic topcoats, together with a standard Navy vinyl-alkyd system for control purposes. These systems were exposed at a deep ocean site and in shallow water. They were rated in the customary manner for blistering, rusting, etc., but no electrical properties were obtained in these evaluations. Although for the present investigation it would have been more desirable to work with pigmented organic coatings rather than with the zinc

inorganic silicate primers, such systems were not planned for immediate evaluation tests. It was not known, of course, whether the zinc inorganic coatings with their probably higher potentials would have any different effect on the outcome of the results.

The exposure conditions in the second series of experiments were essentially the same as those previously reported.¹¹ Different instruments were, however, used for the electrical measurements. For most of the AC measurements a capacitance bridge was employed which was much more accurate than the previously used impedance bridge, especially at the frequencies higher than 1 kc which were used in the dissipation factor versus frequency measurements.

In this present series of experiments, DC resistance measurements were also made. The method was modified from that of Bacon⁴ and of Brown⁵ as described in the experimental section. In these measurements the electrical system composed of the steel panel, the coating system, sea water, and a calomel electrode, was considered to be a cell with high internal resistance. This internal resistance was the resistance of the coating, and it was measured by determining the open cell potential and the potential of the same cell when closed by a shunt of approximately the same resistance as the coating system.

The DC resistance measurements were of particular interest because a qualification procedure involving DC resistance measurements has recently been proposed by the Pacific Naval Laboratory for the use of the Royal Canadian Navy. The method, as described by Anderton and Brown¹⁴ uses the method previously reported by Brown.⁵ One of the requirements of the qualification procedure is that the resistance of coated panels immersed in flowing sea water for one year does not fall below ten megohms, or 10^7 ohms.

The DC resistances of coatings that have been reported in literature have been much higher than the AC resistances recorded in the literature or found in previous experiments at this Laboratory. Similar differences were found in the present experiments, as further noted below. The DC resistances were higher than the AC resistances by factors of from 26 to 260,000. Part of the reason for the differences in values no doubt is due to the fact that the DC resistance values were only indirectly obtained and may not be the true DC resistances.

In the calculation of the DC resistance of the coating from the values of the open cell potential (E_o) and the shunted cell potential (E_s), obtained as shown in Figure 21, it is assumed that there is no change in the basic electromotive force (E) as current is drawn from the cell. Thus, for the

shunted cell, it is assumed that the effective potential across the internal resistance (E_i) is the difference between the basic electromotive force of the cell and the measured potential across the shunt resistance, and therefore is the difference in the two measured potentials, or that

$$E_i = E - E_s = E_o - E_s$$

In the shunted cell, the currents through R_i and R_s are the same because the current through the electrometer is negligible, and thus

$$\frac{E_i}{R_i} = \frac{E_s}{R_s}$$

Substitution of the first equation in the second equation gives:

$$R_i = \left(\frac{E_o - E_s}{E_s} \right) R_s$$

The implied assumption that there is no change in the basic electromotive force of the cell is not correct. There will be a drop in the potential, E , due to polarization (and possibly due to other factors) and the total driving force during shunted measurements will be less than E_o . The change in the measured voltage that is due to the change in resistance will therefore be less than the measured change, and the internal resistance of the cell will therefore be smaller than the value calculated from the above equation.

Some Russian investigators have used the term ohmic resistance and polarizing resistance. From the abstracts available it is not quite certain whether these two resistances added together correspond to the DC resistance as calculated above. In one article an ohmic resistance of approximately 20% was reported¹⁵ and in another article an ohmic resistance of approximately 2 to 5% of the total resistance.¹⁶ If the ohmic resistance is essentially the same as the AC resistance, then the ohmic resistances of the panels studied in the present experiments vary from 4% to less than one thousandth of 1% of the total DC resistance. Irrespective of the actual significance of the DC resistances as calculated, the object of the present experiments was to determine whether the values obtained could be correlated with coating performance, and whether they would be significant in the prediction of coating performance.

Performance of the Coating Systems

The performances of the coating systems used in this second series of experiments were much better than the performances of the systems used in the first experiment. Part of the reason was that inherently better coating systems were employed and part of the reason was that much thicker coatings were used. Thus, after exposure in the ocean at a depth of 6800 feet for 13 months or after exposure in aerated sea water at 25°C for two years, these coatings had essentially perfect ratings with only two exceptions. One of these was System S14 (vinyl) which developed moderately dense blistering under both exposures. The other was System S16 (epoxy) which generally developed one large blister on each panel but was otherwise in excellent condition. After 1-½ years of exposure in shallow sea water the results were similar, except that Systems S17 and S18 developed some blisters in the topcoat only. The latter could have been partially caused by heavy barnacle attachment to the soft hydrocarbon topcoat.

One of the coating systems was essentially the same in both series of experiments but was applied at a thickness of only 6 mils in the first series and at a thickness of 11 mils in the second series. This was the Military Specification vinyl-alkyd system which was System 3 of the first series of experiments and the control system, C1, in the second series. This system maintained relatively steady AC resistance values which were approximately twice as high as those of the previously exposed thinner coating system.

One of the coating systems, S19, had not only a zinc inorganic silicate primer but also an inorganic topcoat. This coating system was different from all the other coatings in its performance and electrical characteristics. The system had a comparatively high electrical conductivity, or low resistance, during the entire duration of the experiment. Although this system gave good protection for the period of the experiment, the coating itself eroded away or flaked off as time progressed. Nevertheless, no rusting or blistering or damage to the substrate was noted. Its protective action apparently was different from that of the other coatings, and electrical methods of testing performance do not appear to be applicable to this type of coating.

For the measurement of the electrical properties, the panels were brought into the laboratory and were placed into a salt water bath which was accurately maintained at 25°C. Due to a malfunction of the regulator of the bath, the temperature at one point rose to a value high enough to melt the ceresin edging, or to a temperature of at least 60°C. Most of the panels showed no signs of damage, however, the aluminum filled hydrocarbon topcoats of Systems S17 and S18 appeared to have been slightly damaged, especially at a few points where the warm ceresin apparently dissolved portions of the topcoat. For these two systems, there were definite drops in the DC resistances. For the vinyl-alkyd system there was a small drop in the DC resistance. The AC resistances were not very appreciably affected.

Although for most of the systems the accidental overheating had no apparent effect, the possibilities of such effects were considered in all comparisons of electrical properties and performance. The exposure times at which the brief overheating occurred are shown in the graphs, and none of the conclusions are based on results obtained after the panels had been overheated.

Most of the coating systems on prolonged exposure in the flowing sea water became discolored with a brown deposit. This discoloration was considerably greater in areas that were exposed to direct sunlight. The rate of discoloration was reduced when the small building in which the panels were housed was darkened by blocking the windows. The possibility was therefore raised at the deposits were biological growth. However, examination showed that there were some diatoms, plankton, and bacteria, but that by far the predominant amount of the deposit was organic debris. The latter could have been very fine material which was not retained by the filter system through which the sea water was supplied.

AC Measurements

The AC resistance values in general remained at a higher value during this series of experiments than in the previous set, as might be expected for coatings of higher performance. Comparatively low values leveling off at approximately 30 k Ω were shown by System S16 (epoxy). System S14 (vinyl), which was the only other system showing blistering, had AC resistance values close to 100 k Ω . The highest AC resistances were those of the vinyl-alkyd control system, which maintained resistances above 1 megohm.

AC resistance measurements were obtained for two panels of each system. The first panel was immersed approximately 250 days before the second panel. The resistance values of the two panels at the same exposure time were in fairly good agreement and differed from each other by less than 30%, with only few exceptions. The exceptions included System S17 (hydrocarbon), for which the first and second panels showed considerably reduced resistances beginning at about 250 and 125 days, respectively, after the overheating of the bath. This overheating may or may not be responsible for these delayed effects. A slightly greater deviation of 50% was shown by the vinyl-alkyd system, C1, but only during the period of between about 100 and 350 days. This slightly increased deviation may also be due to the overheating of the bath, which for this particular system appeared to cause approximately a 25 to 50% increase in AC resistance.

The second panel of the inorganic system, S19, had a resistance which at the beginning was approximately 50% greater than that of the first panel. Both sets of resistances continued to climb until the bath overheated and

these resistance values then dropped, or leveled off and dropped. The maximum value reached by either panel was, however, only 50 ohms, which is a resistance much too low to contribute to the protection of the coating.

In general, the changes in the capacitance curves were the inverse of the changes in the resistance curves. As the resistances become lower, the capacitances increased, but the changes were not as great. The capacitances were lower for the vinyl-alkyd control system, C1, and for the epoxy top-coated System S15. The capacitances were higher than average for the aluminum-filled hydrocarbon coatings, and they were very high for the inorganic system, S19.

For most of the systems the capacitances and the resistances changed considerably immediately after immersion. This change presumably is related to the water uptake of the coating system. Water uptake increases the capacitance and decreases the resistance, the latter change being the more pronounced. Very little initial change was noted for Systems S17 and S18 (with hydrocarbon topcoats) which therefore have less water uptake.

The initial changes in capacitance and resistance are indicated in Figures 2 to 8. The initial values (that is, the first readings obtained) are shown by arrows at the ordinate scales. The 24-hour values (or the closest readings thereto) are the first points plotted on the curves.

Dissipation factors were also measured with each of the AC resistance and capacitance measurements. The dissipation factor is a measure of the conductive component of the current in a capacitor, and the coating system on a panel immersed in sea water is essentially the dielectric of a capacitor. The current in a capacitor is illustrated in Figure 20. The dissipation factor (D), the loss tangent ($\tan \delta$), the loss current (I_i), the charging current (I_c), and the resistance and capacitance are related as follows:¹⁷

$$D \equiv \tan \delta = \frac{I_i}{I_c} = \frac{1}{WRC}$$

Since the decreases in resistance were greater than the increases in capacitance, the dissipation factors generally increased with exposure. The changes were less than the changes in resistance but greater than the changes in capacitance. To conserve space, the curves of the dissipation factors are not reproduced herein.

It had been claimed that the dissipation factor-versus-frequency curves obtained for a coating immediately after immersion in water would be a good indication of the long term performance of the coating.^{6,7} For the five coating systems that were exposed in the first experiments at this Laboratory no such relationship appeared to exist.¹¹ In the present series of experiments, there, however, appeared to be some relationship. If System S19, the inorganic system which has a very high dissipation factor, is disregarded, then System S14, which showed the greatest blistering in immersion tests, had by far the highest dissipation factor at the various frequencies. (High dissipation factors and a steep slope for this curve are claimed to be characteristic of poorer coatings.) The slope of the curve for System S14 (vinyl), as shown in Figure 9, is however not appreciably greater than that of the other curves. The dissipation factor-versus-frequency curves shown in Figure 9. were obtained after 3 hours of immersion. For System S15 and S16 (with epoxy topcoats) these curves rose considerably during the progress of the experiments and after several hundred days they were higher than the curve of System S14 which had not risen very appreciably. For the remaining Systems, S17, S18, and C1 there were no very appreciable changes in the curves.

DC Measurements

DC electrical measurements were obtained for three panels of each coating system. Two of these panels had been the same ones for which AC electrical measurements were made. The third panel was used for DC measurements only. The reason for not subjecting one panel of each set to AC measurements was to prevent any undue effects which might possibly be caused by connecting a relatively low DC resistance to the panel. During the AC conductance measurements the electrical network is such that the panels are subjected to a DC resistance of approximately 200 k Ω . This value is much smaller than the shunt resistances generally used in the DC measurements and it was not known whether connecting such a comparatively low resistance might affect the panel. However, there appeared to be no differences in the DC resistances of the second and third panels that could be related to any effects of the AC measurements.

The variations in DC resistance values were much greater than the differences in the AC resistance values. Whereas different panels in the same system exposed for the same period of time showed differences of 30% in the AC measurements, corresponding DC resistance values differed from each other by as much as factors of 100. Such high differences were obtained for panels which had been subjected to similar conditions of immersion. Even greater differences were obtained in some cases when, for the equivalent exposures, panels subjected to overheating were compared with panels that had not been subjected to overheating.

One reason for the sometimes large differences in DC resistances for different panels of the same system, and for the fluctuations in the resistance of one particular panel may be the effect of polarization. As was pointed out above, a major portion of the difference between AC and DC measurements may be due to this polarization. A comparison of AC and DC resistances for one panel of each system is shown in Table 3. Initial DC resistances obtained up to 2 hrs after immersion and initial AC resistances obtained up to 4 hrs after immersion are shown, as well as the comparative DC and AC resistances obtained after approximately ten days of immersion, when the values changed less rapidly. The latter resistances vary by factors of from 26 to 130,000. If polarization really plays such a large part in the measurements, major fluctuations in the calculated resistances would not be too surprising.

Brown pointed out that in his experience, when the AC resistance values were below about 10^5 ohms, there was not very much difference between AC and DC resistance values, and that the polarization effects were therefore not very large. Brown further pointed to an AC resistance of 10^5 ohms as being more or less a plateau. In the present experiments, however, most of the AC measurements were above 10^5 ohms and some were as high as 1.4×10^6 ohms. With the bridge that was used, measurements of resistances of this magnitude appeared to pose no problem. Because of the apparent limitation in measurements of AC resistances above 10^5 ohms, Brown felt that DC measurements were more accurate. Whether this is in fact true in the present experiment, or whether polarization provides an even greater error in the DC measurements is not known.

In the qualification procedure proposed by Anderton and Brown,¹⁴ a requirement is that all three panels exposed in sea water for one year maintain DC resistance values of 10 megohms or greater. The shape of the panels employed by Anderton and Brown is slightly different from the shape of the panels used in the present studies and the coating area of nominal thickness which was exposed in their studies was approximately 140 sq cm as compared to 120 sq cm. This is a ratio of 1.17 to 1 and the smaller panels used in the present experiment should therefore have higher minimum resistances which should be about 1.2×10^7 ohms.

The conductive coating, S19, of course, did not meet the above requirements. The resistances of the panels of System S16 (epoxy) fell considerably below this value. The first panel of System S14 (vinyl) barely met this requirement, but the first panels of all the other systems, that is, S15, S17, S18, and C1, definitely met this requirement. (The second and third panels of these systems, which were subjected to overheating at about 90 days, did not always meet this requirement. Thus one panel of S14 and S18 did not meet the requirements, and both the second and third panels of S17 fell below 1.2×10^7 ohms before the end of the one-year exposure period.)

The DC resistance of the first panel of System S14 was so close to limiting value that it is questionable whether 3 panels would all have qualified under this procedure. It thus appears that 4 of the 6 non-conductive coatings would definitely have passed the qualification procedure. (if the second and third panels had not been subjected to overheating). These 4 systems are System S15, S17, S18, and C1, and these systems all showed no deterioration in exposures to aerated sea water at 25° for periods of up to 2 years nor in the deep sea immersion at 6800 feet for 13 months.

The minimum DC resistances that were recorded are listed in Table 4. The values before overheating and after overheating are given. The first set of values given is therefore for measurements at up to 350 days for the first panel and up to 94 days for the second and third panels. The second set of values listed in Table 4 is for subsequent exposure periods and these may or may not have been affected by overheating.

The potentials of the panels with respect to a calomel electrode, or in other words the open cell potentials, varied considerably as shown in Figure 19. The minimum values were approximately 0 and the maximum potentials were approximately -1.0 volt. Individual panels showed variation of as much as 0.8 volts. The inorganic zinc silicate coatings may have been partly responsible for the large potentials and for the large variations in potential. However, even the vinyl-alkyd control coating showed considerable variation and the highest single value was 0.7 volts greater than the minimum value. The latter system also showed considerable variation in the calculated DC resistance values and the high potentials of the zinc inorganic silicate coatings therefore do not appear in themselves to be responsible for fluctuations in the resistance values.

Permeability

It has been stated that there is no definite relationship between the permeability of a coating and its performance.¹⁸ However, in the previous set of experiments, with five coating systems of widely differing performances, there did appear to be an inverse relationship between permeability and performance. It was reasoned that permeability probably would be a contributing factor and that large differences in permeability probably would affect performance. In this second set of experiments, the two systems that performed less well did not have significantly different permeabilities. Therefore, no relationship between permeability and performance could be established.

General Considerations

The above results have shown that organic coatings which perform well maintain high AC and DC resistances. To what degree electrical measurements can predict long term performance has not been established because no long term performance data for these systems is yet available. Two corollary questions are whether electrical measurements give indications of poor performance sooner than does visual inspection and whether electrical measurements give indications of poor performance more accurately than does visual inspection.

Of the six systems that originally had high AC and DC resistances, four systems maintained high resistances and showed essentially no deterioration (except in one instance some blistering that may have been caused by barnacle attack). Two systems developed low AC resistances which dropped below about 100 k Ω and DC resistances which dropped below about 10 megohms. These were S14 (vinyl) and S16 (epoxy). The first of these developed some blisters before the resistances dropped to the above values. (However, the slopes of the DC resistance curves, after the first ten days, were steeper than those of any other system having high resistances.) The second of these systems developed no blisters or other visual defects until after there was a strong drop in resistance.

One problem with visual inspections is that the results in the early stages of deterioration can not be accurately used to predict performance. Furthermore the ASTM rusting and blistering ratings are somewhat subjective and considerably more variable than the electrical measurements. Thus a panel may show light blistering at one visual inspection but may not show blistering at a subsequent visual inspection.

A further problem with visual inspections is the fact that there are no good methods for describing performance. In evaluations performed by NCEL personnel, it appears that the degree of blistering is the best available indication of long term performance. However, for some systems with considerable blistering, the protection rating remains very high because no actual deterioration of the substrate has taken place.

Whether electrical measurements give better indications of projected performance than does visual inspection can not be ascertained at this point. There is the possibility that better indications can be obtained sooner by a combination of the two methods.

To compare the results of electrical measurements with long term performance, a third set of experiments has been started with coating systems that have been evaluated over a longer period of time for use on steel piling.

For this comparison, the same coating systems that had been evaluated earlier were duplicated on the small panels for immersion in sea water and electrical measurements.

CONCLUSIONS

1. Four of the systems investigated maintained calculated DC resistance values appreciably above 10 megohms and these systems have shown very little deterioration in exposure tests conducted to date. These systems would therefore appear to pass the qualification requirements that have been proposed for the Royal Canadian Navy and the results to date would appear to justify the use of such a qualification procedure. Two systems had resistances which dropped to approximately 10 megohms or lower after one year and these systems generally showed greater deterioration in exposure tests.
2. The same four systems which showed very little deterioration had AC resistances which remained above 100 k Ω . For two of the systems the resistances dropped below 100 k Ω and these were the systems which showed blistering in the exposure tests. Thus there appears to be a relationship also between the AC resistance and coating performance.
3. One of the seven systems was highly conductive and it appears that for such systems no predictions can be made on the basis of electrical measurements. (None of the conclusions reached are therefore based on results with this system.)
4. The changes in capacitance of the systems were not sufficiently great to allow any conclusions to be drawn regarding a possible relationship between capacitance and performance.
5. The two systems which developed blistering and performed less well had dissipation factor-versus-frequency curves somewhat higher than those of the four systems that performed better. However, especially in view of the previous lack of correlation of dissipation factors with performance, the differences in dissipation factors do not appear to be sufficiently great to establish any correlation with performance.
6. There appears to be no correlation between permeability and performance.
7. The exposure tests must be continued for a longer period of time to determine whether the electrical measurements can predict long-term performance.

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The performance by Mr. E. J. Miller of most of the experimental work is gratefully acknowledged. The coating of the panels in connection with other evaluation tasks by Mr. A. F. Curry and the furnishings of evaluation results in deep and shallow water obtained by Messrs. C. V. Brouillette, R. L. Alumbaugh, and A. F. Curry are appreciated.

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Table 1. Coating Systems

System	Description of Systems	Thickness (mils)	
		of coating	of system
S14	Zinc inorganic silicate (post-cured)	2.0	
	Vinyl iron oxide and chromate primer	1.5	
	Vinyl mastic intermediate	4.0	
	Vinyl finish	1.5	9.0
S15	Zinc inorganic silicate (self-cured)	4.0	
	Catalyzed epoxy lead-silico-chromate primer	2.0	
	Catalyzed epoxy intermediate	5.0	
	Catalyzed epoxy-polyamide finish (gray)	2.5	13.5
S16	Zinc inorganic silicate (self-cured)	4.0	
	Acrylic zinc chromate, zinc oxide primer	1.0	
	Catalyzed epoxy finish (gray)	8.5	13.5
S17	Zinc inorganic silicate (self-cured)	3.0	
	Modified phenolic-epoxy red iron oxide primer	1.0	
	Aluminum-pigmented hydrocarbon resin finish	6.5	10.5
S18	Zinc inorganic silicate (post-cured)	2.0	
	Modified phenolic-epoxy red iron oxide primer	1.0	
	Aluminum-pigmented hydrocarbon resin finish	6.5	9.5
S19	Zinc inorganic silicate (self-cured)	3.0	
	Inorganic finish (gray)	3.5	6.5
C1	MIL-P-15328B (Formula 117), pretreatment	0.5	
	MIL-P-15929B (Formula 119), vinyl red-lead primer	6.0	
	MIL-E-15936B (Formula 122-27), vinyl-alkyd finish (gray)	4.0	10.5

Table 2. Performance of Coating Systems

System	Blistering Rating After Exposure Indicated ^{a/}			
	Aerated Sea Water at 25°C		Shallow Sea Water	Deep Ocean at 6800 ft.
	<u>1 year</u>	<u>2 years</u>	<u>1½ years</u>	<u>1 year</u>
S14	6F	4MD	2MD	2MD
S15	10	10	10	10
S16	2F ^{b/}	2F ^{b/}	2F	2F ^{b/}
S17	10	10	2M ^{c/}	10
S18	10	10	2M ^{c/}	10
S19	10	10	--	10
C1	10	10	10	10

^{a/} ASTM method D714-56.

^{b/} One very large blister or group of blisters but no other blisters.

^{c/} In topcoat only.

Table 3. Comparison of AC and DC Resistances

<u>System</u>	<u>Resistances Obtained Initially</u> (ohms)			<u>Resistances After About Ten Days</u> (ohms)		
	<u>DC</u>	<u>AC</u>	<u>Ratio</u>	<u>DC</u>	<u>AC</u>	<u>Ratio</u>
S14	2.7×10^9	323 k	8,400	1.1×10^9	183 k	6,000
S15	1.6×10^{10}	1400 k	11,000	5.3×10^7	204 k	260
S16	4.2×10^8	709 k	590	4.5×10^6	174 k	26
S17	1.9×10^9	263 k	7,200	2.5×10^9	252 k	9,900
S18	1.0×10^{11}	295 k	260,000	4.9×10^{10}	369 k	130,000
S19	1.6×10^3	6.4	250	3.0×10^3	4.7	640
C1	1.5×10^{10}	1600 k	9,100	3.6×10^9	1090 k	3,300

Table 4. Minimum DC Resistances

System	Minimum DC Resistance Before Overheating	Time of Last Readings before overheating	Minimum DC Resistance After Overheating
	(ohms)	(1st set, 2nd set)	(ohms)
S14	1.3×10^7	350 da., 94 da.	3.8×10^5
S15	4.2×10^7	346 da., 93 da.	9.2×10^7
S16	1.0×10^5	333 da., 92 da.	3.2×10^4
S17	4.0×10^8	332 da., 90 da.	1.5×10^5
S18	6.9×10^9	331 da., 87 da.	2.1×10^6
S19	1.5×10^3	325 da., 84 da.	1.5×10^3
C1	1.8×10^8	339 da., 85 da.	5.1×10^8

S14-25
616 days

S14-26
382 days

S14-27
382 days



Figure 1. Panels of System S14.

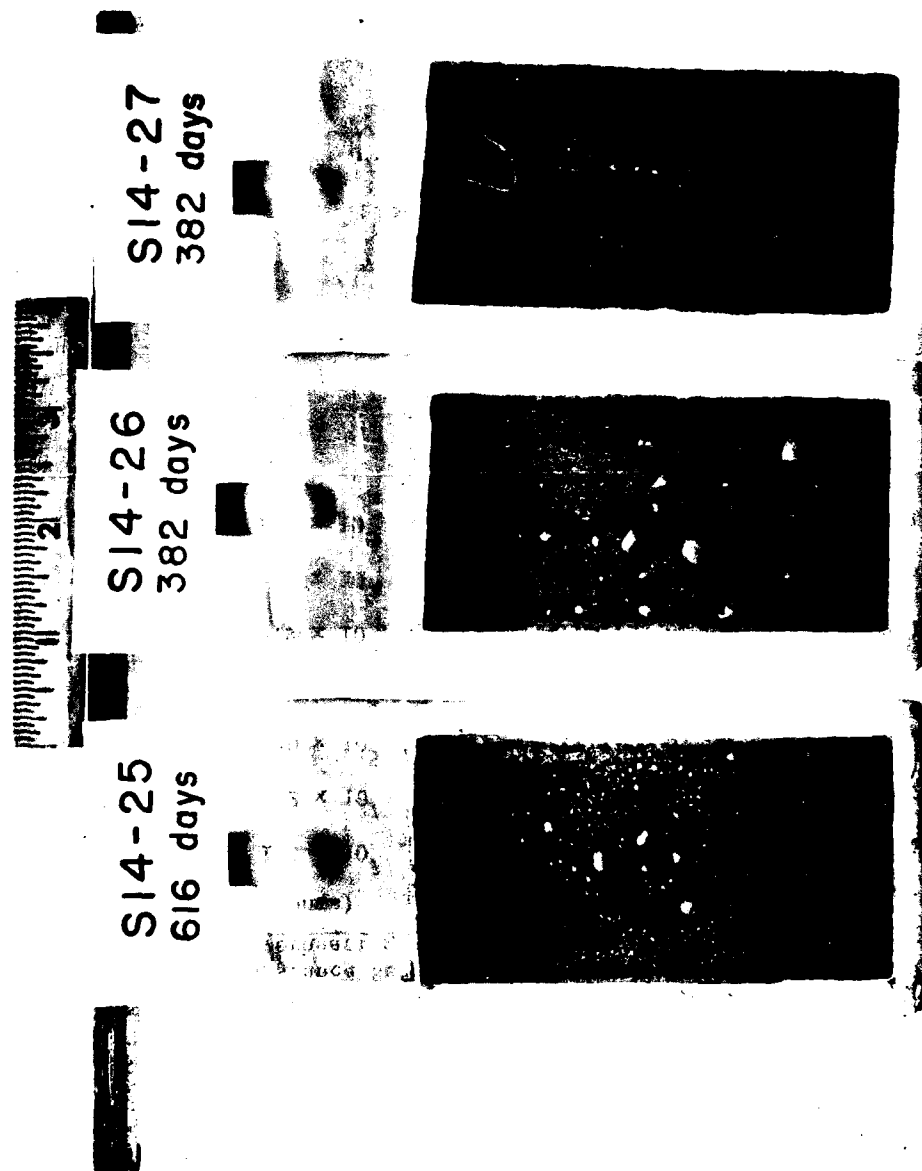


Figure 1. Panels of System S14.



Figure 2. Panels of System S19.

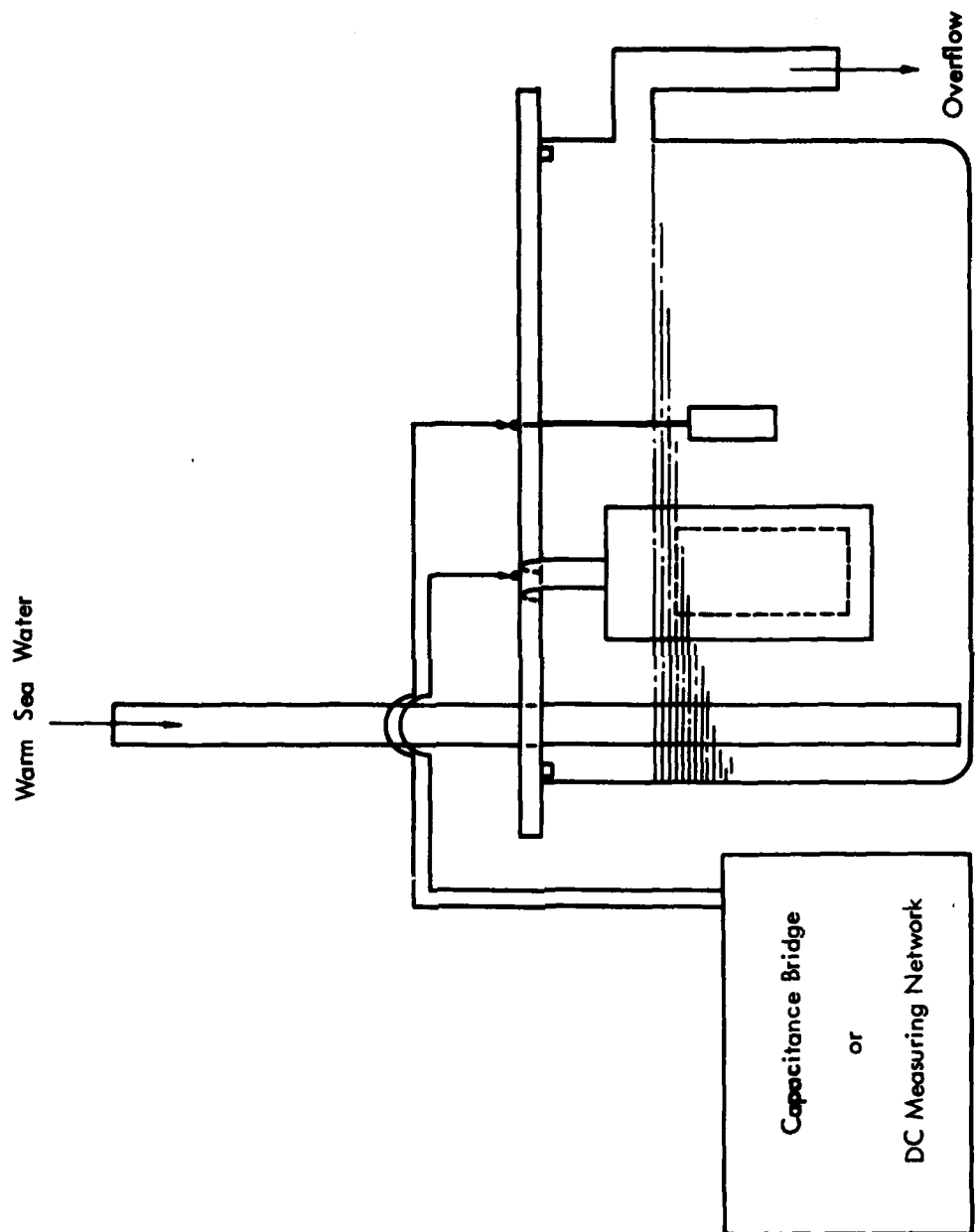


Figure 3. Experimental set-up (schematic).

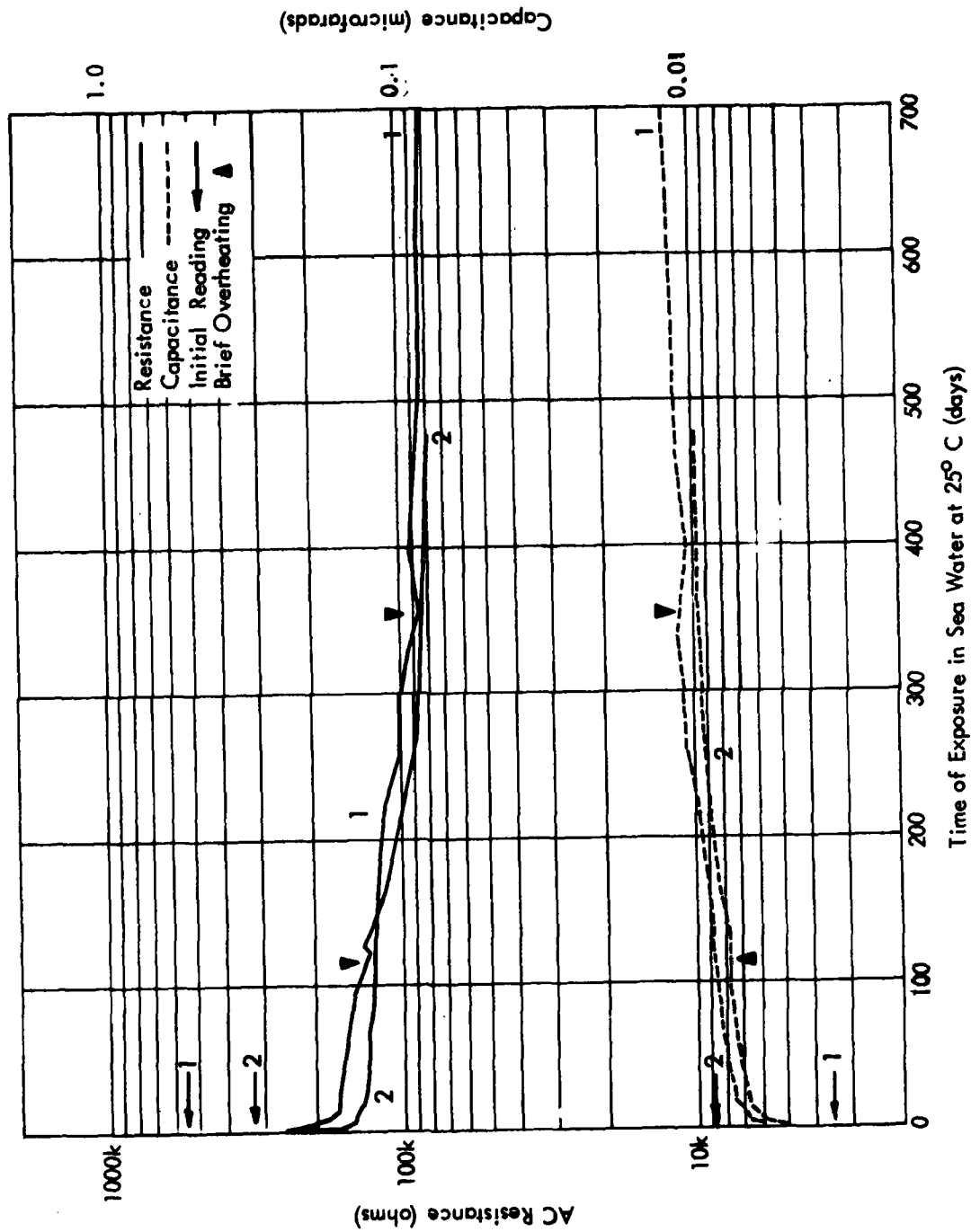


Figure 4. AC resistance and capacitance of System SL4 (vinyl topcoat).

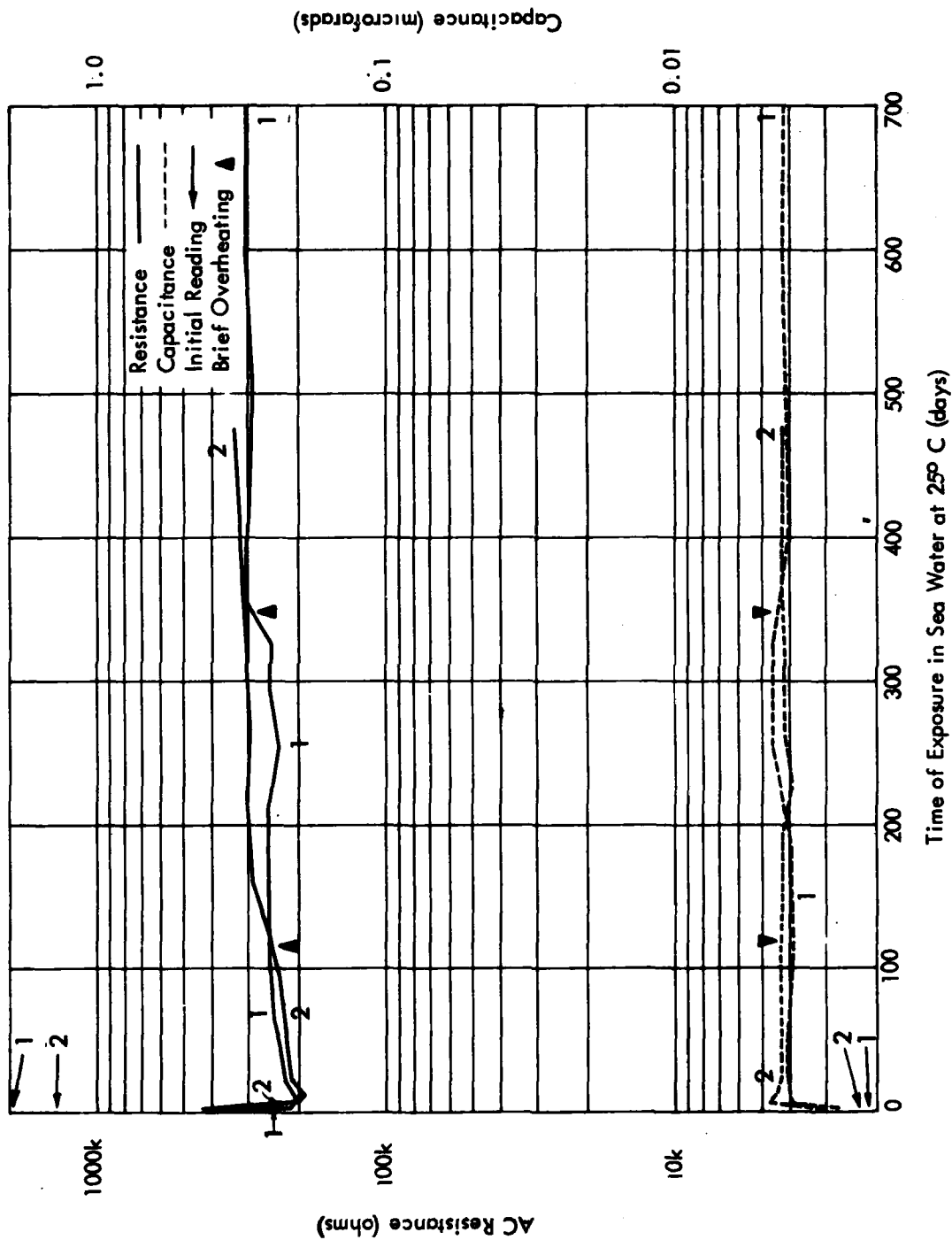


Figure 5. AC resistance and capacitance of System SI5 (epoxy topcoat).

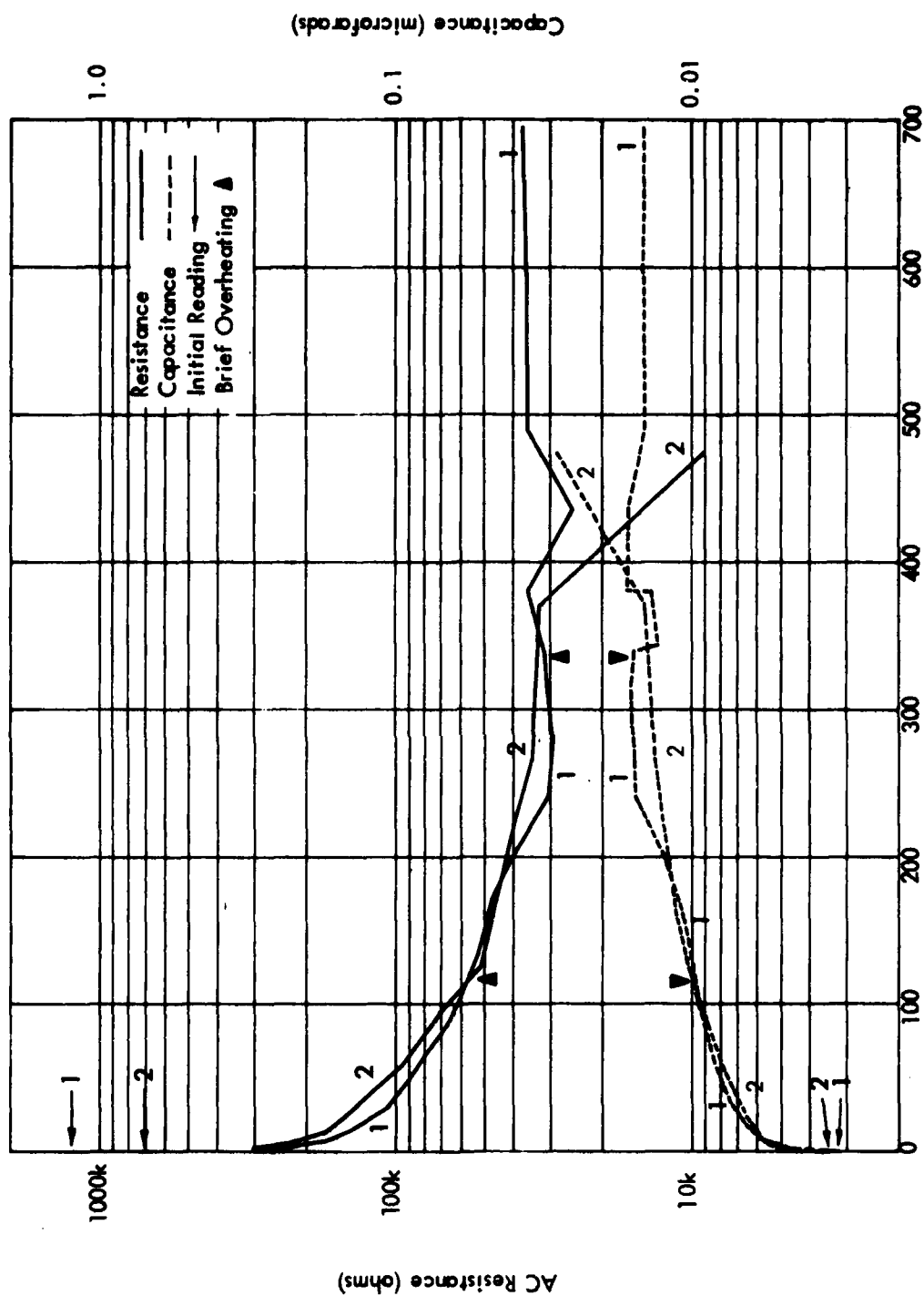


Figure 6. AC resistance and capacitance of System S16 (epoxy topcoat).

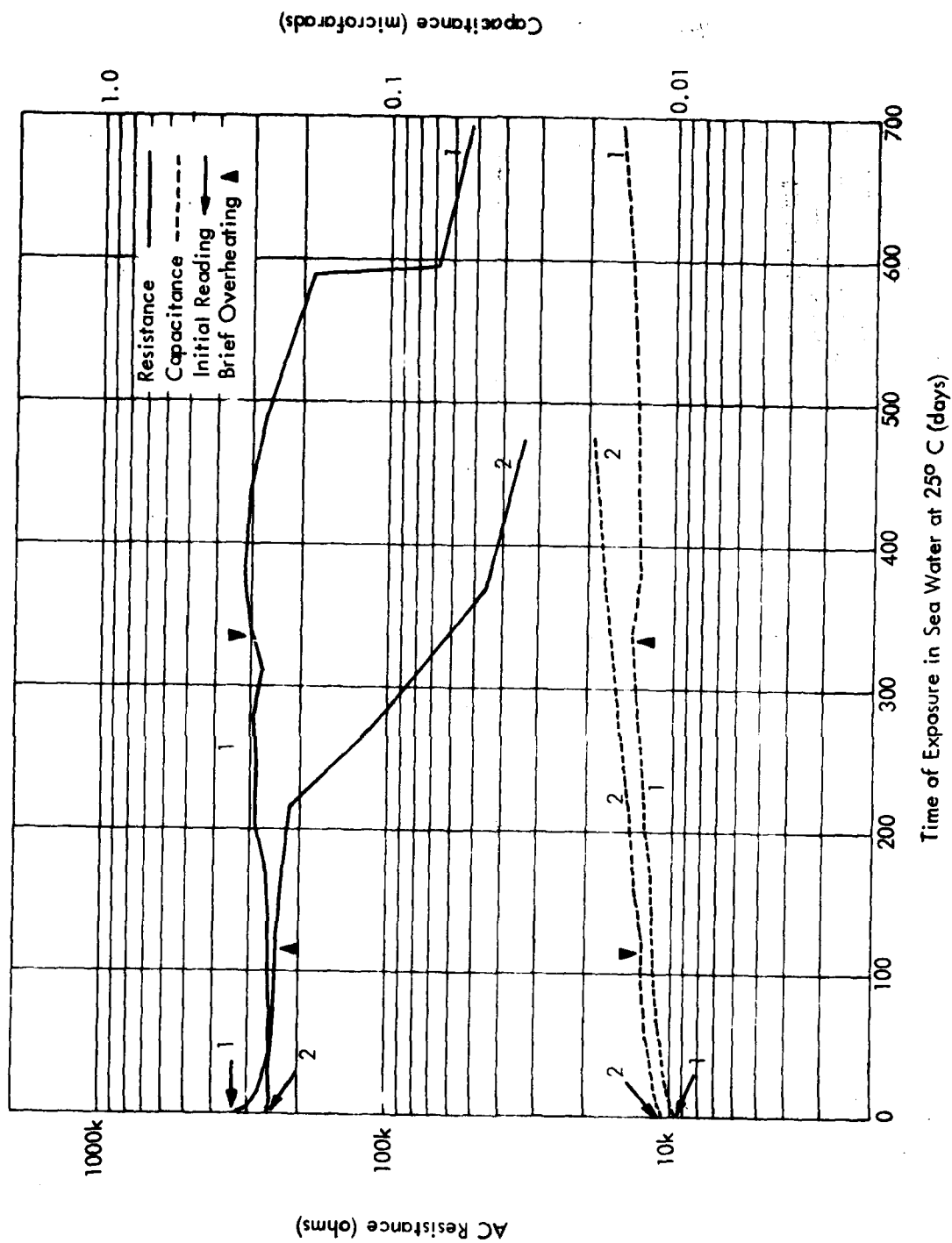


Figure 7. AC resistance and capacitance of System S17 (hydrocarbon topcoat).

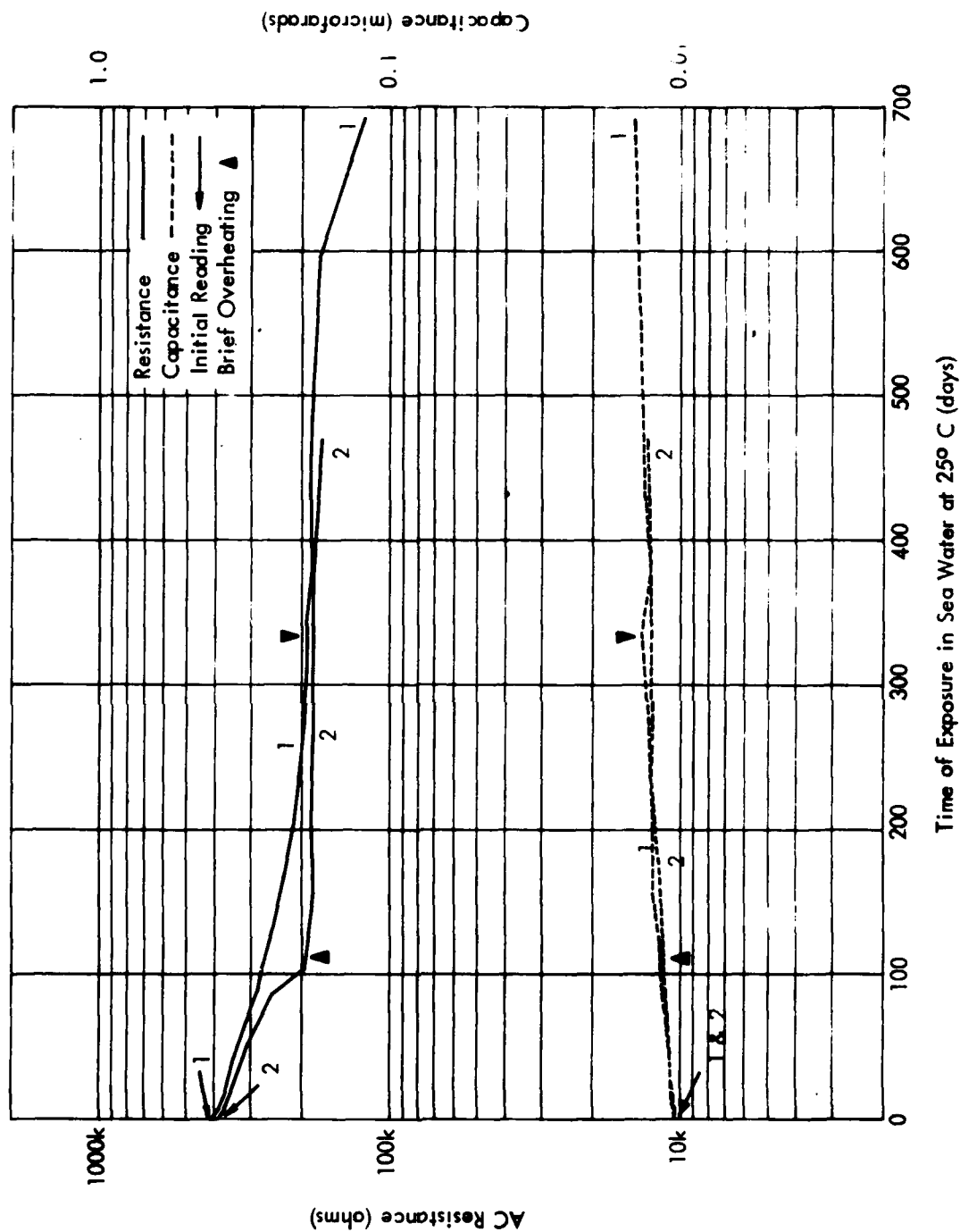


Figure 8. AC resistance and capacitance of System S18 (hydrocarbon topcoat).

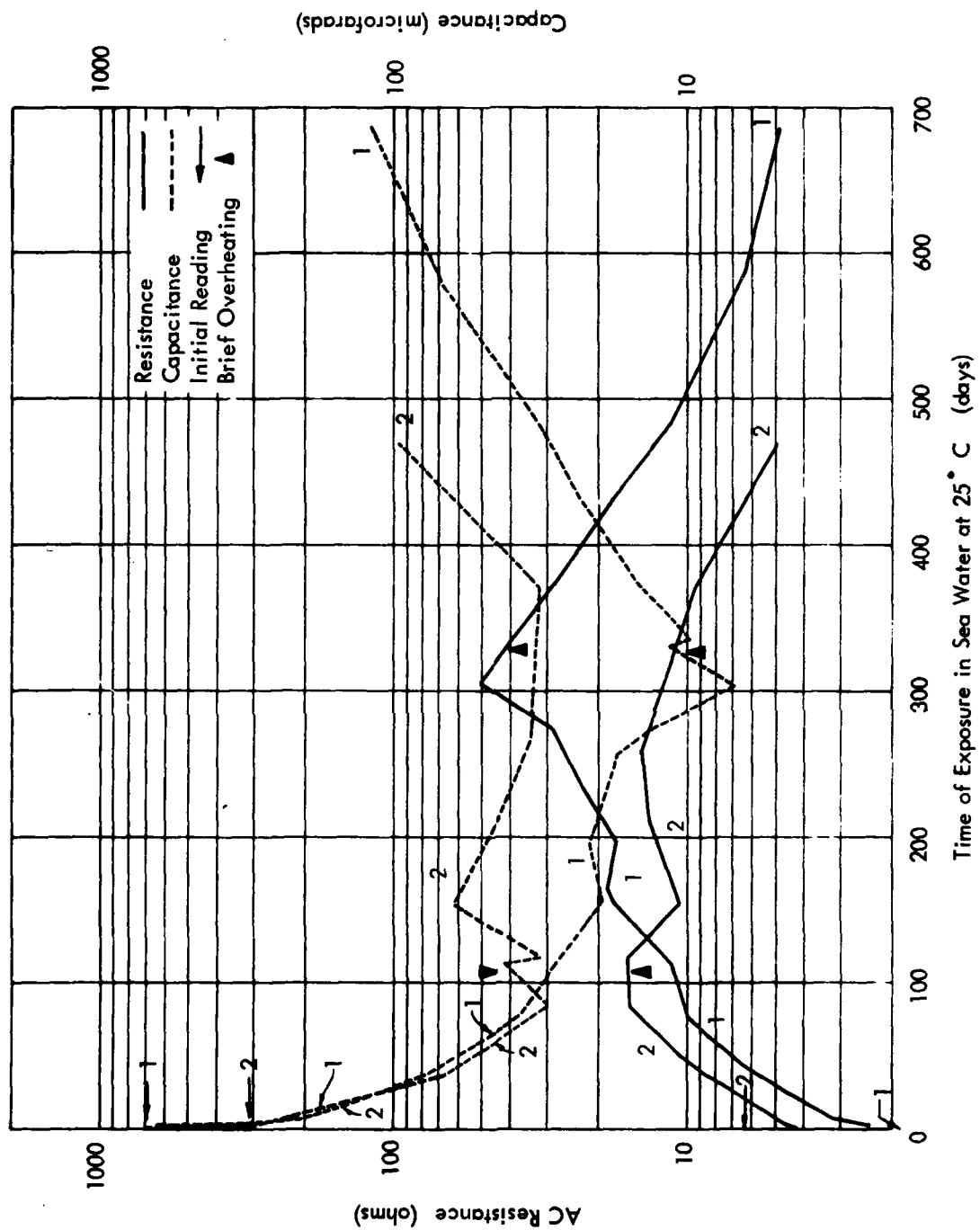


Figure 9. AC resistance and capacitance of System S19 (inorganic topcoat).

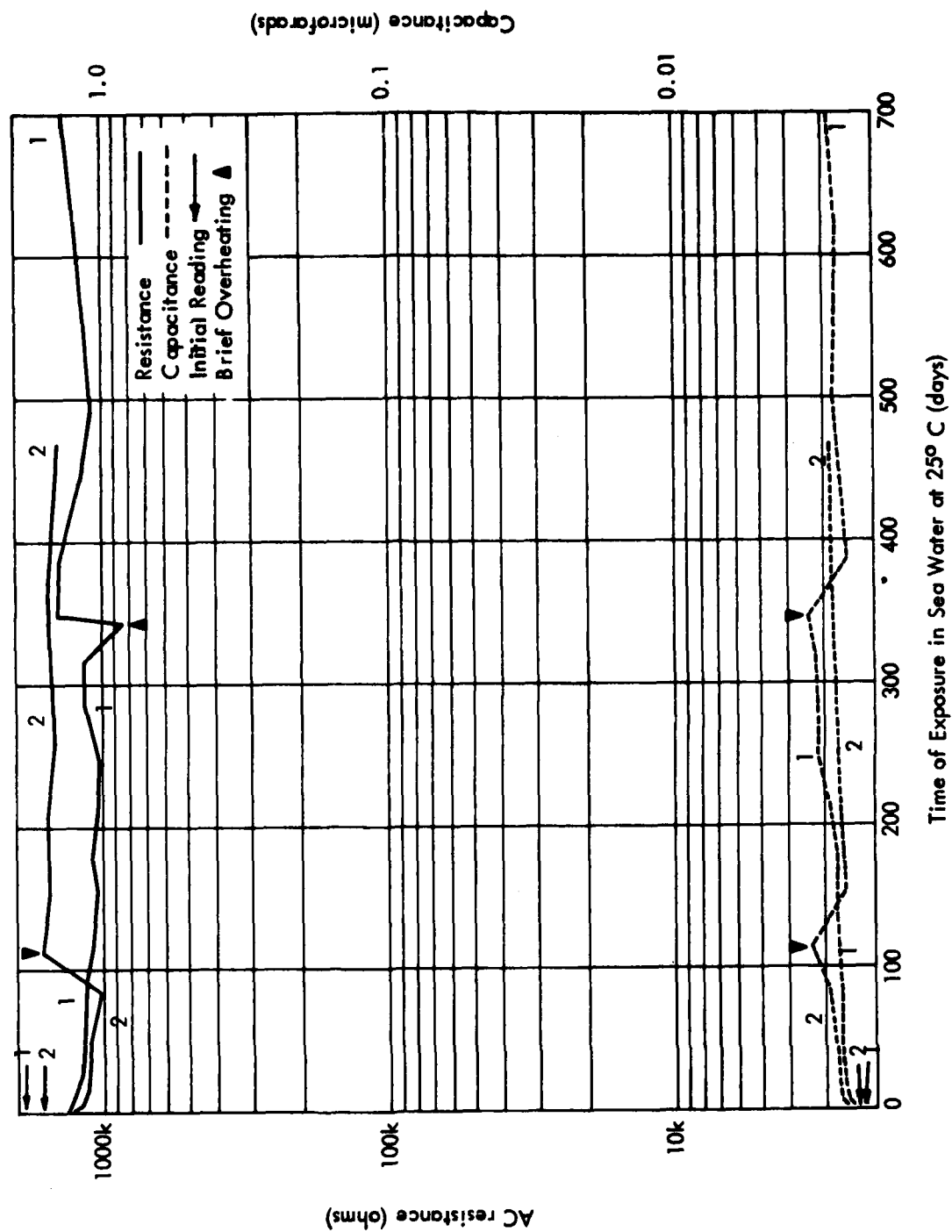


Figure 10. AC resistance and capacitance of System C1 (vinyl-alkyd system).

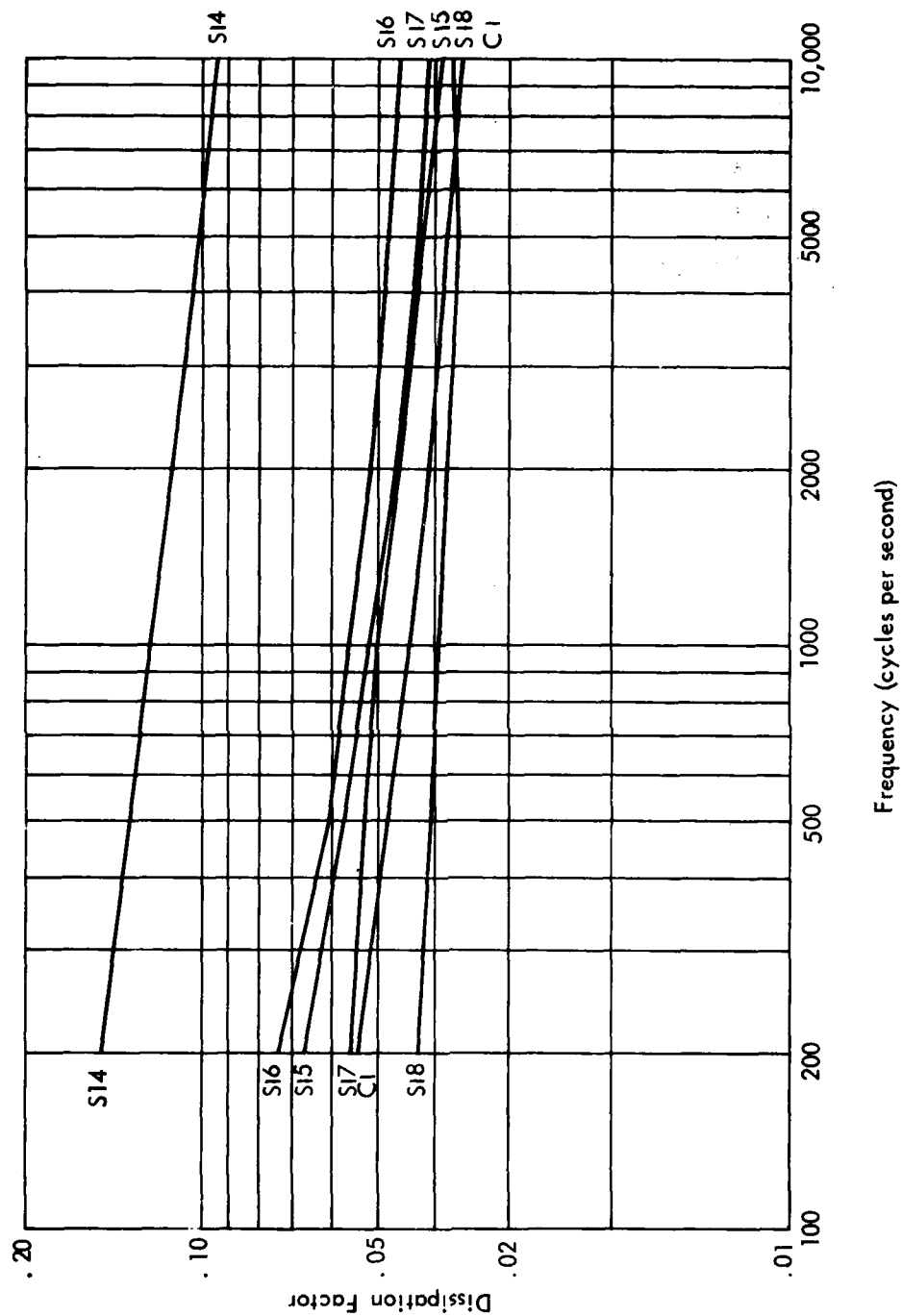


Figure 11. Dissipation factors at different frequencies.

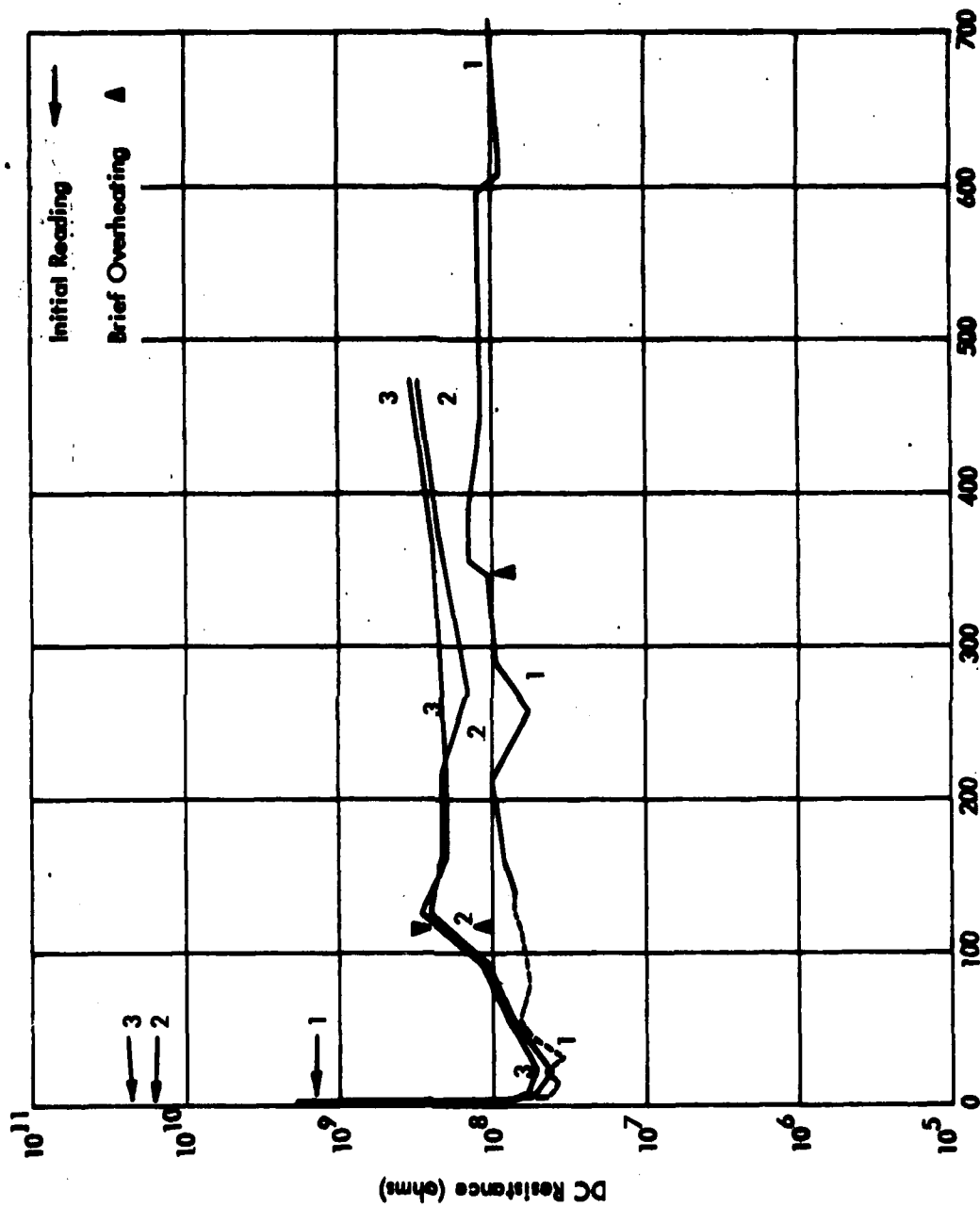


Figure 14. DC resistance of System S15 (epoxy topcoat).

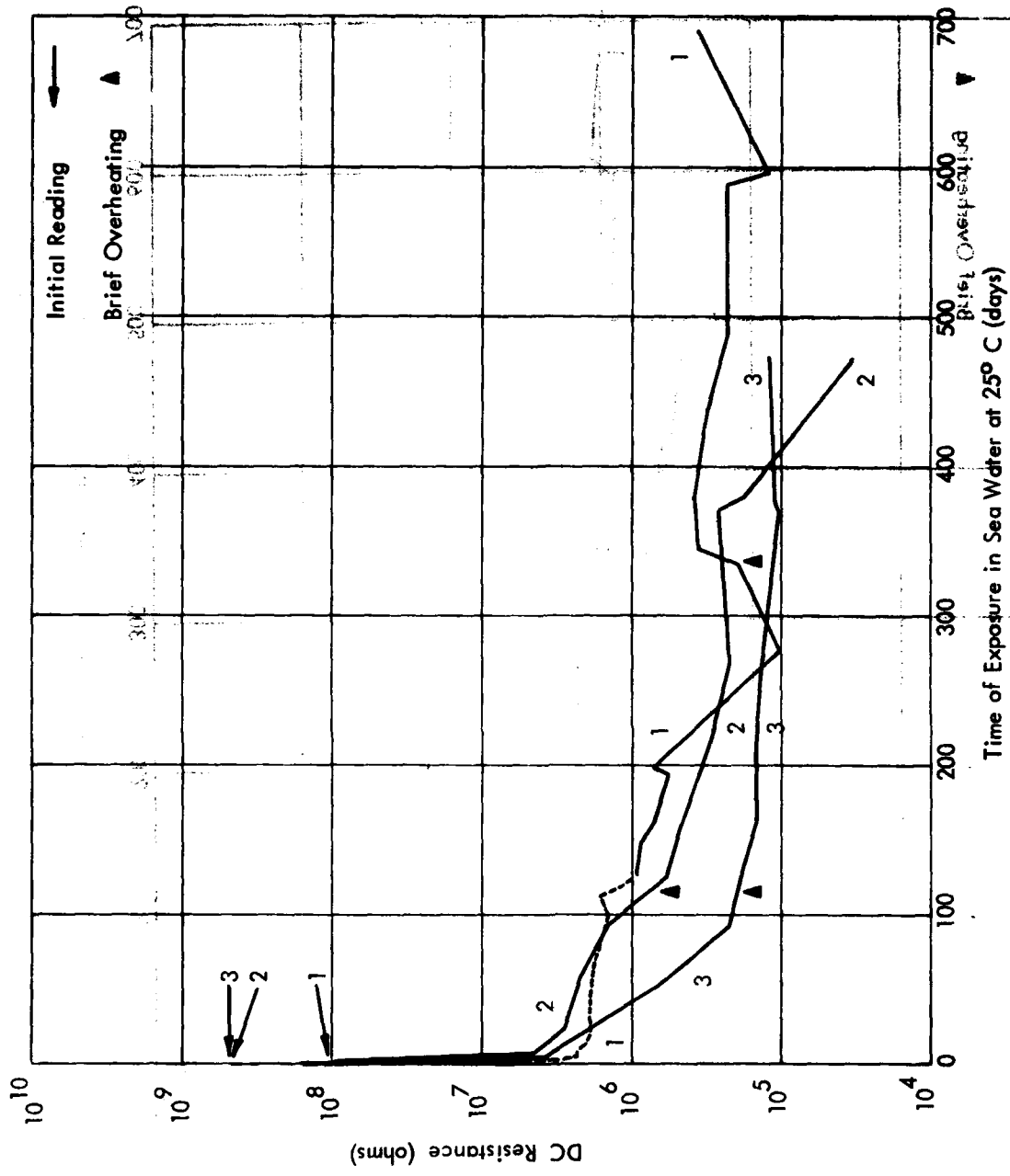


Figure 15. DC Resistance of System S16 (epoxy topcoat).

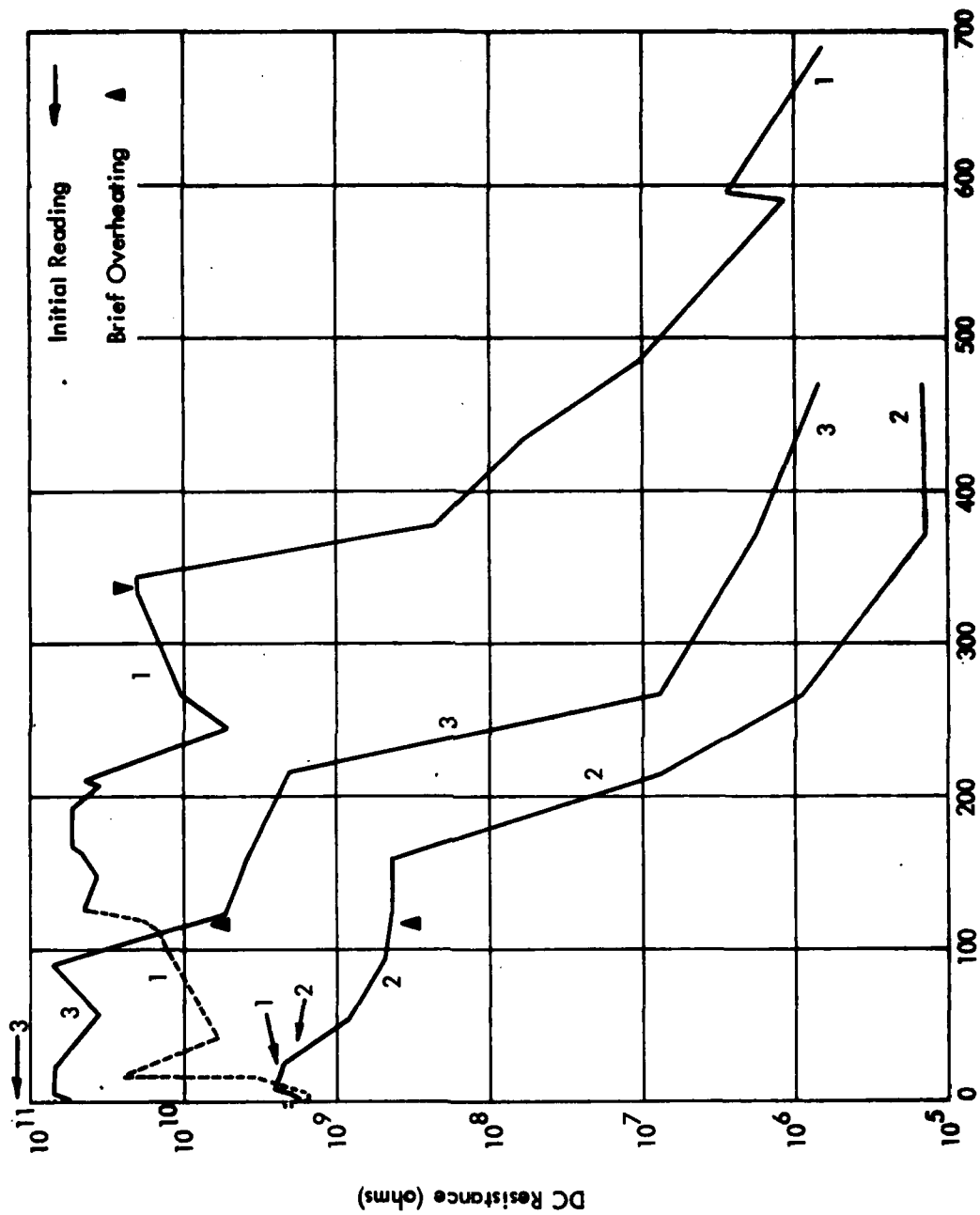


Figure 16. DC resistance of System S17 (hydrocarbon topcoat).

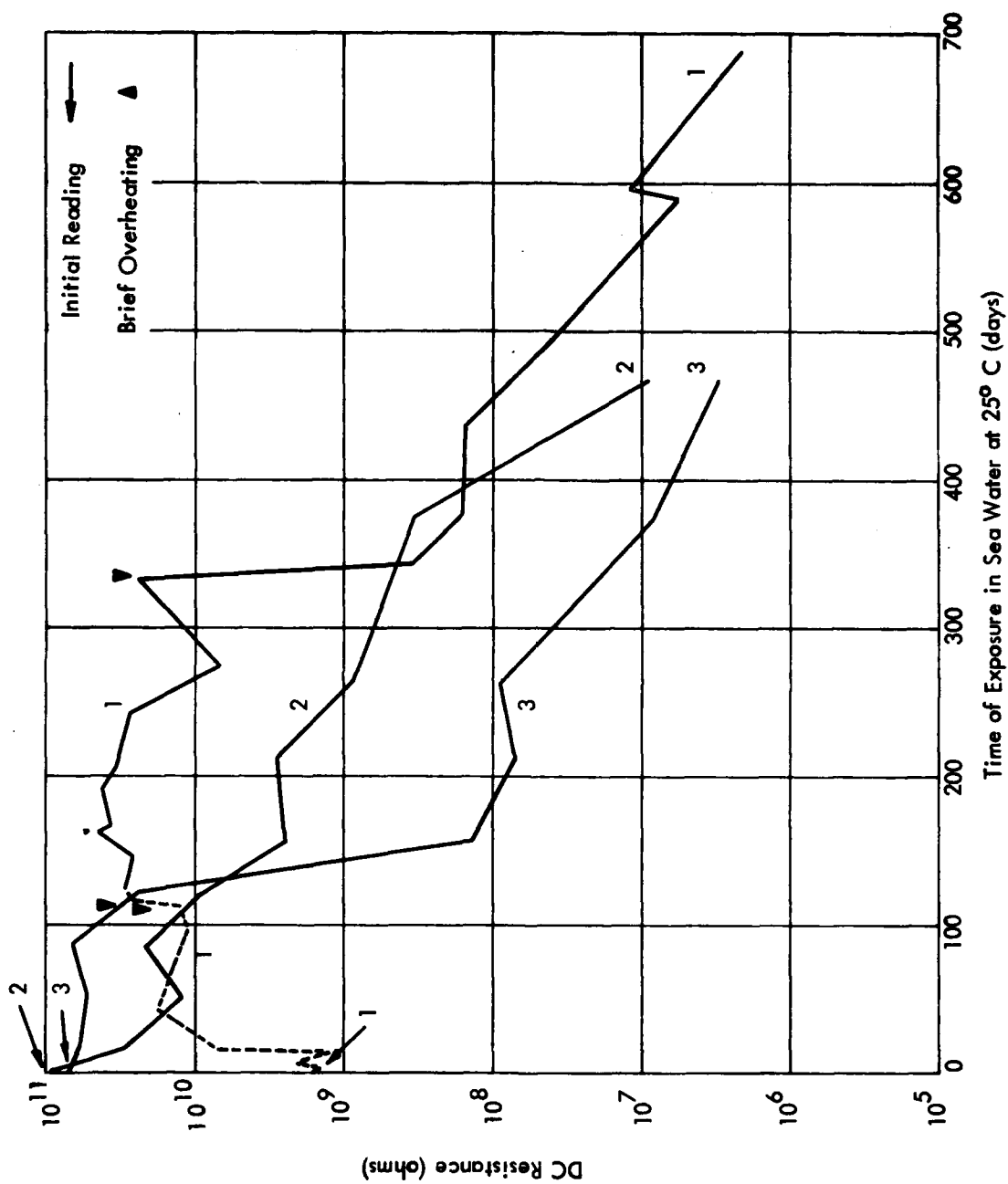


Figure 17. DC resistance of System 518(hydrocarbon topcoat).

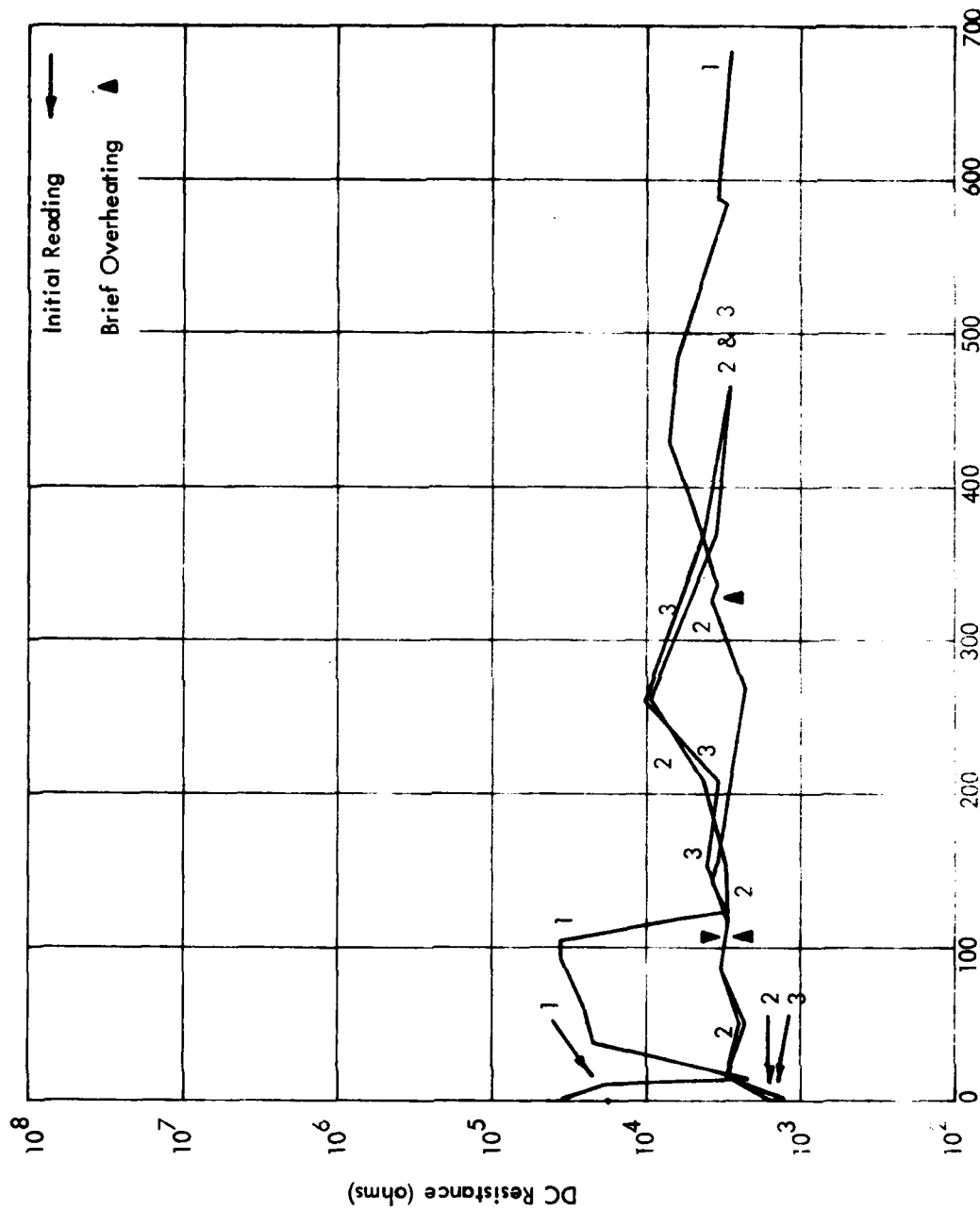


Figure 18. DC resistance of System 519 (inorganic topcoat).

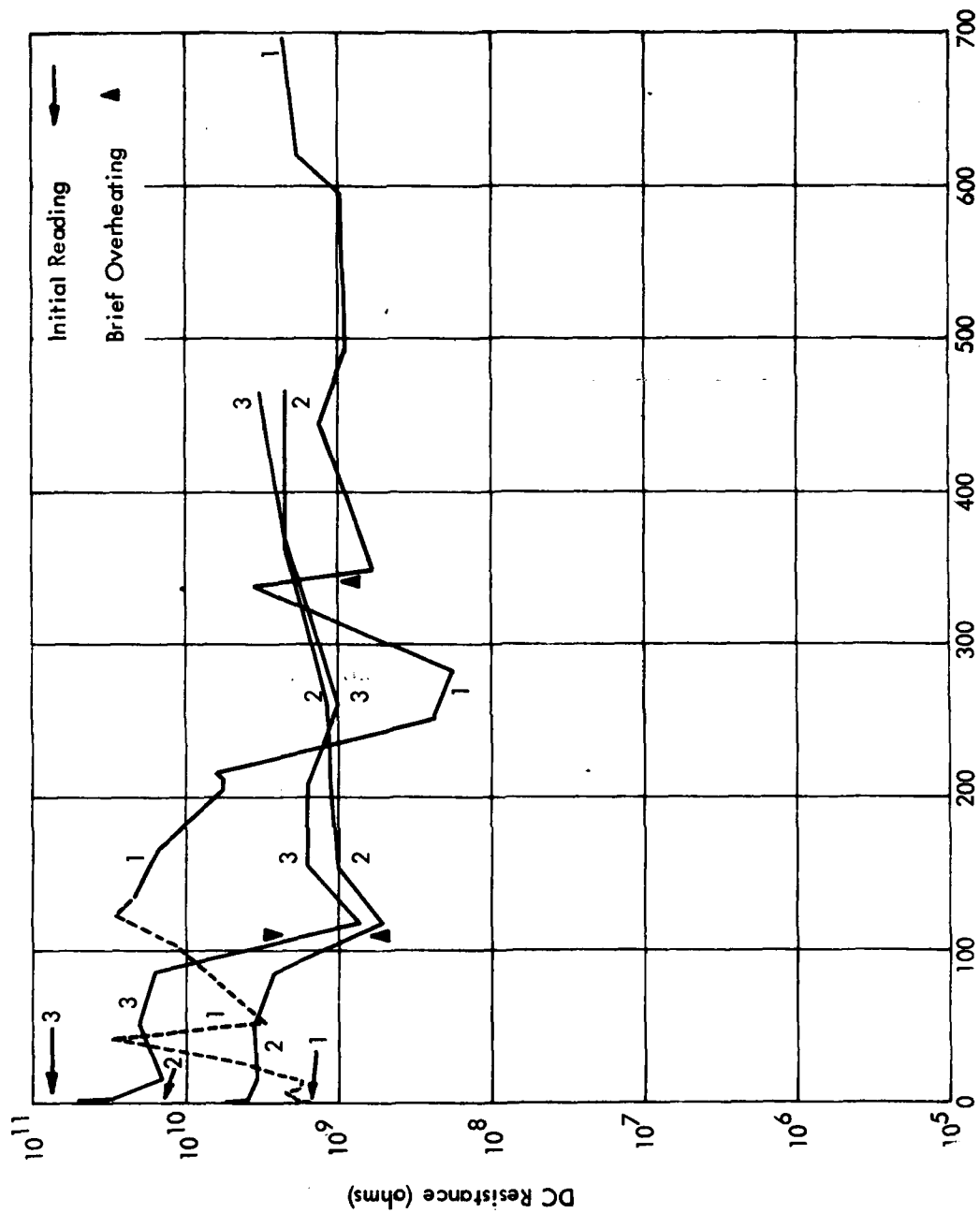


Figure 19. DC resistance of System C1 (vinyl-alkyd system).

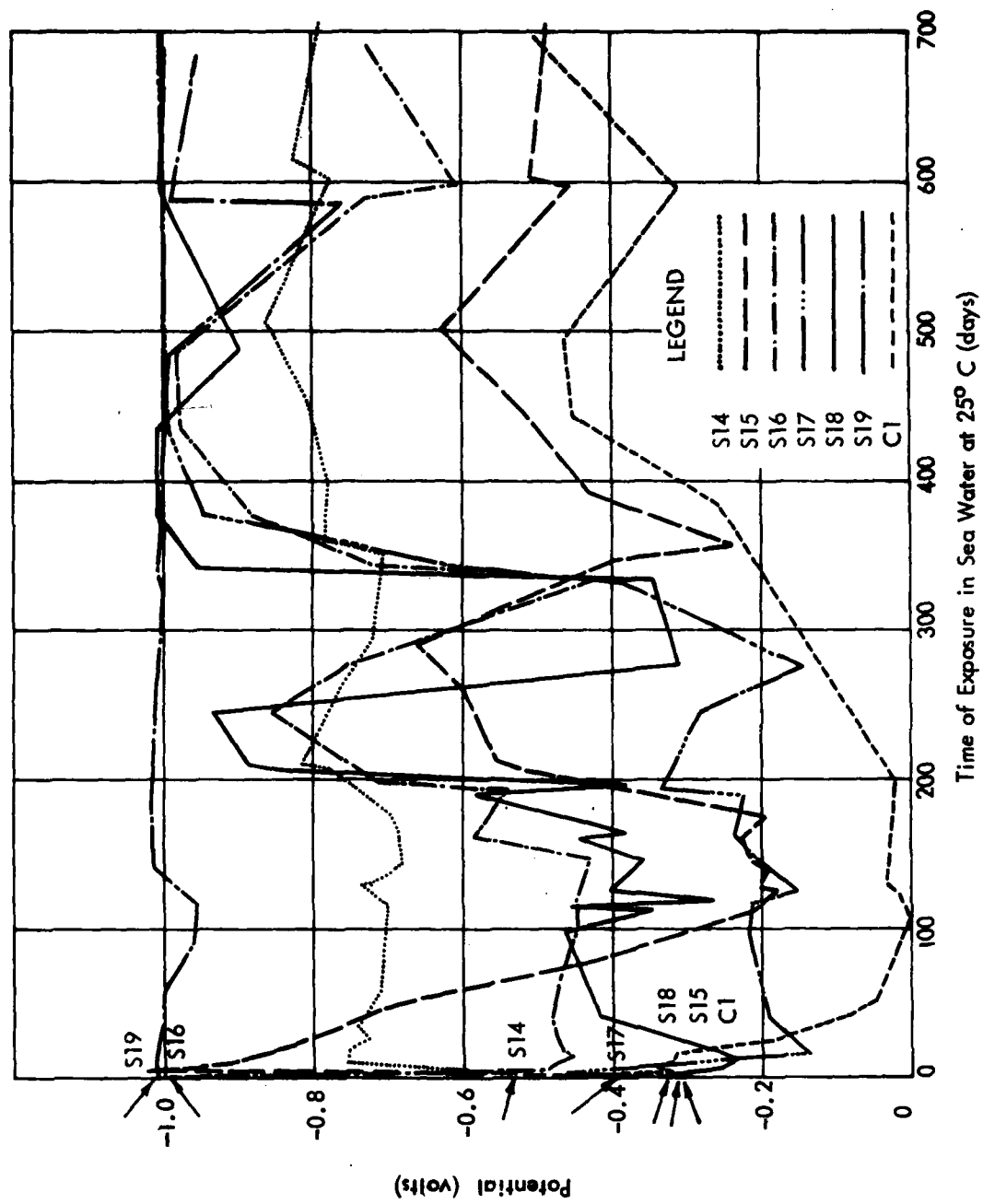


Figure 20. Open cell potentials.

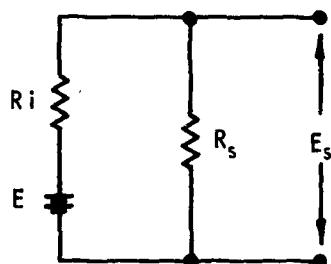
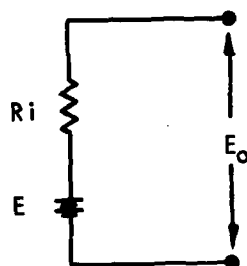
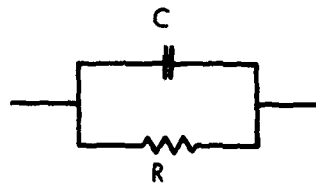


Figure 21. Open and closed cell potentials (schematic).



effective network of a capacitor

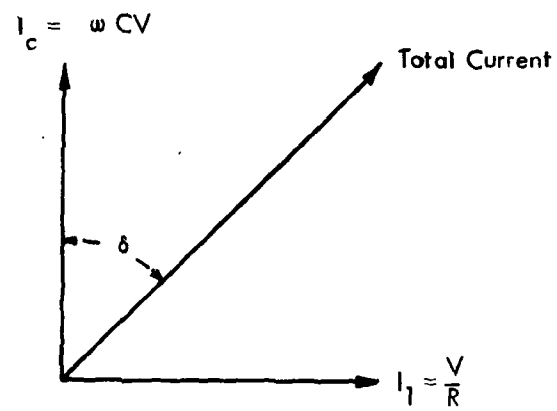


Figure 22. Current in a capacitor.

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<p>Seven coating systems on steel panels were immersed in salt water for up to nearly two years. AC and DC electrical properties of the coatings were determined and were compared with the performance of the coatings in the laboratory, in shallow water, and in the deep ocean. Four of the systems showed comparatively little deterioration, and these coatings maintained high AC and DC resistances. Two systems which showed greater deterioration in exposure to sea water had high resistances initially, but subsequently developed lower AC and DC resistances. One system, consisting only of inorganic coatings was very conductive and its electrical properties thus could not be related to performance. Long term performance data for correlation with electrical measurements are not yet available. No definite relationship between dissipation factors of the coating systems and performance could be established, nor could a relationship between water permeability and performance be established.</p>		

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